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PHASE AND STRUCTURAL EVOLUTION DURING MECHANICAL MILLING AND SUBSEQUENT ANNEALING OF HIGH-ENTROPY AlCuNiFeCr ALLOY

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High entropy alloys (HEAs) are a new generation alloys and are quite different from traditional ones, which are based on one or two elements. HEAs defined as alloys that generally have at least 5 major metallic elements and each of which has an atomic percentage between 5 % and 35% have attracted increasing attentions. According to the regular solution model, the alloys have very high entropy of mixing, which makes HEAs usually form BCC and/or FCC solid solutions rather than intermetallic compounds or other complex ordered phases [1]. A number of these high entropy alloys have been developed for both functional applications, and have demonstrated favorable combinations of strength, ductility, oxidation resistance, and thermal stability [2]. So far, various techniques have been adopted to synthesize HEAs, such as vacuum arc melting, rapid solidification, coating, and mechanical alloying (MA) [3]. MA is a widely used solid state processing route for synthesis of advanced materials, which can easily lead to the formation of nanocrystalline and will definitely increase the properties and application scope of high entropy alloys [1]. In this paper, AlCuNiFeCr high-entropy solid solution alloy was synthesized by MA, and the structural evolution during milling and subsequent annealing processes were investigated. The as-milled powder was consolidated by pressure sintering and the structure and microhardness were investigated too.

Elemental powders of Al, Cu, Ni, Fe, Cr, in equiatomic ratio were used as the starting mate-rials for MA. Milling of elemental powders was carried out up to 5 h in high energy planetary ball mill with ball to powder weight ratio of 10:1. The powder samples were extracted at intervals of 0,5; 1; 2; 5 h during milling. The 5 h ball milled alloy powder was then heat treated 1 h at different tem-peratures under flowing high purity argon atmosphere. Then, ball milled alloy powder was consoli-dated by pressure sintering at 800 °C for 30 min at a pressure of 5 GPa. X-ray diffraction (XRD) was performed with Rigaku Ultima IV X-ray diffractometer with Cu K_α radiation to analyze struc-ture and phase evolution during milling, subsequent annealing at temperatures ranging from 500 to 1000 °C and after sintering. The chemical compositions of the milled powders were calculated from the results of energy-dispersive X-ray spectrometer (EDX) equipped with SEM. The thermal analy-sis was carried out in a STA449F1 differential scanning calorimeter (DSC) at a heating rate of 20 K/min under flowing purified argon atmosphere. Vickers hardness measurement of the consolidated samples was performed with a Micro Hardness Tester HV-1000 under a loading of 1,5N and a dura-tion time of 15s. The reported hardness value is an average of at least twenty measurements.

Fig. 1shows the XRD patterns of the equiatomic AlCuNiFeCr high-entropy alloy powders prepared under different milling durations. The primitive blending powder includes diffraction patterns of all alloy elements. Drastic decrement of diffraction intensity is observed after 0.5 h of milling. Many diffraction peaks can hardly be seen after be ball milled for 1 h. The disappearance of diffraction peaks can be seen as the beginning of the solid solution formation. Only the most intense diffraction peak can be clearly seen in the 2 h ball milled powder, which indicates the complete formation of BCC solid solution structure (β-phase). As the milling time reaches up to 5 h, the diffraction peaks exhibit no change except for a broadening. The intensity decrement and peak broadening in the diffraction can be attributed to the formation of nanocrystalline and high lattice strain induced by mechanical deformation during the MA processing [4]. Alloying occurs when the grain

sizes of the elemental components decrease down to nanometer range and then a substantial amount of enthalpy can be stored in nanocrystalline alloys due to the large grain boundary area. The crystalline size is greatly refined as the milling duration increases. The crystal size of the alloy powders under different milling times have been calculated from the X-ray peak broadening using Scherrer's formula after eliminating the instrumental contribution. The 5 h MA powder exhibits a crystal size of 18 nm.

The MA powders with milling duration higher than 2 h show simple solid solution structure, which can be attributed to the formation of supersaturated solid solution. The solid solubility extension is introduced by: the effect of high mixing entropy [1] and the non-equilibrium state of the MA process. As the component number increases, the random diffusion between different elements will be enhanced and thus the solid solubility is extended. In addition, the high-entropy of mixing can lower the tendency to order and segregate, and so makes the solid solution more easily formed and more stable than intermetallics and other ordered phases [3].

The EDX microanalysis results (not listed in this paper) exhibit the chemical homogeneity and the equiatomic composition of alloy particles after 5 h of ball milling.

Fig. 2 shows the DTA curve of the 5 h mechanically alloyed AlCuNiFeCr powder.

The 5 h, MA powder exhibits exothermic/endothermic trends in the temperature range of 30-1430 ºC. The endothermic peak at 72 ºC is associated with energy absorption which can be related to the evaporation of process controlling agent (PCA) and gas. The long exothermic line in the temperature range of 120 to 550 ºC is associated with the release of internal stresses, such as structural deformation, lattice strain, etc. This exothermic line in the DTA curve demonstrates the recovery and recrystallization processes under isothermal annealing. Fig. 3 shows that after annealing at 500 ºC, the XRD pattern exhibits small FCC peaks along with original BCC peaks. The DSC results shown in Fig. 2 clearly reveal that there is no predominant endothermic or exothermic peak up to 550°C, which indicates that there is no phase change in the nanocrystalline equiatomic AlCuNiFeCr HEA up to 550 °C. This suggests that the small fraction of FCC phase observed in the annealed samples possibly existed in the as-milled condition itself. However, the small volume fraction of FCC phase is not visible in the as-milled condition due to the peak broadening caused by nanocrys-talline nature of the FCC phase. Moreover, peak broadening caused by nanocrystalline nature of the BCC and FCC phases is the reason for the overlapping of the peaks in the as-milled condition due to severe plastic deformation under MA process. The exothermic peak at approximately 580 ºC is re-lated to the energy release during the phase transformation process. Fig. 3 shows that after annealing at 600 ºC, the XRD pattern exhibits small FCC1(α_1) peaks along with original BCC and FCC peaks. This reveals the precipitation of the FCC1 phase, which corresponds to the sharp exothermic peak at 580 ◦C in the DTA curve. After annealing at 700 and 800 ºC, Fig. 3 shows that the powders exhibit BCC, FCC and FCC1 mixed phases. However, the minor increasing XRD peak intensities of the FCC and BCC phases indicate the grain growth of both phases, which correspond to the exothermic line in the temperature range of 650 to 800 ºC in the DTA curve.

Fig. 3 indicates that after annealing at 900 and 1000 ºC, the powders exhibit both BCC and FCC mixed phases. However, the increasing XRD peak intensities of the BCC and FCC phases indicate the grain growth of both phases. After heating to 800ºC, a long endothermic curve appears and it can be attributed to the gradual collapse of crystalline structure under high temperature. The endothermic peak at 1310 ºC in the DTA curve is designated as the alloys' melting point.

The XRD patterns of nanocrystalline equiatomic AlCuNiFeCr HEA are shown in Fig. 4, which evidences the phases formed in as milled and consolidated conditions, i.e. after 5 h of milling and pressure sintering at 800 °C with 5 GPa pressure for 30 min. The XRD pattern shows the single BCC phase in the 5 h milled sample. The consolidated samples show the BCC phase and a small volume fraction of FCC phase. Obvious peak broadening, shown in Fig. 4, confirm the nanocrystalline nature of AlCuNiFeCr HEA with BCC and FCC structure.

The Vickers's hardness HV of as-consolidated nanostructured equiatomic AlCuNiFeCr HEA has been found to be 9.5 ± 0.2 GPa. The high hardness could be attributed to the nanocrystalline nature of the alloy, the solid solution strengthening equiatomic nature of the phases and the presence of two-phase structure [4] with a larger volume fraction of nanocrystalline BCC phase and minor FCC phase. In general, nanocrystalline structure is expected to enhance the hardness and wear re-sistance of the material.

The entropy of fusion of all the elements in the present system is less than that of the configurational entropy of the five-component system (ΔS_{mix} = 13.38 J·mol^{-1}·K^{-1}), which means the randomness due to the number of elements present in the system is higher than the randomness in the melting. This high configurational entropy (high randomness in the system) and also the large quantity of defects induced during MA may lead to the formation of simple crystal structure in this HEA. The formation of amorphous phase at the equiatomic composition in the present system is not observed, possibly due to the smaller differences in the atomic sizes (δ = 4.9 %).

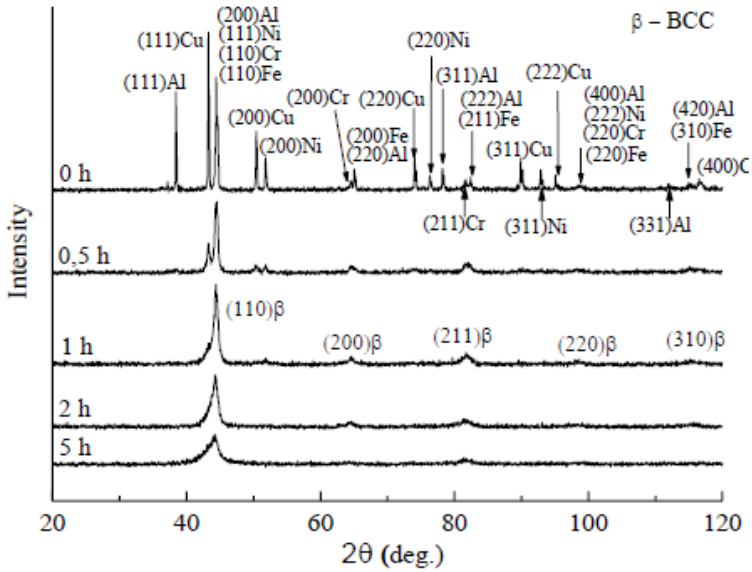

Fig. 1. XRD patterns of mechanically alloyed AlCuNiFeCr powders with different milling times

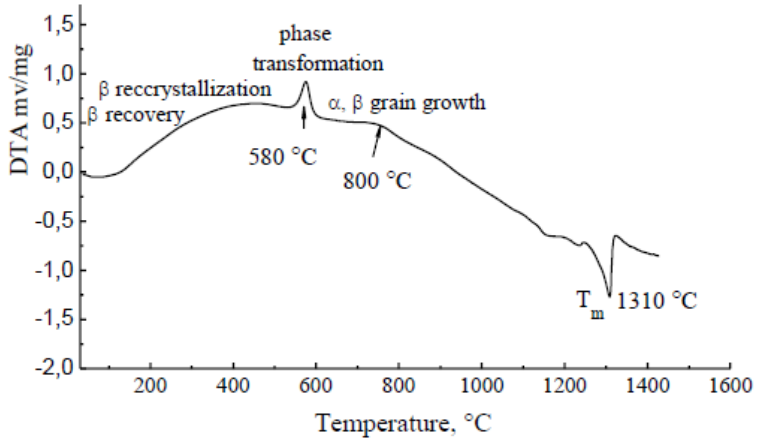

Fig. 2. DTA curve of the 5 h mechanically alloyed AlCuNiFeCr HEA powder

It was justified experimentally that MA of Al-Cu-Ni-Fe-Cr powder mixture during 5 hours resulted in a two-phase nanocrystalline HEA with a structure of BCC and minor FCC solid solutions. During thermal annealing recovery and recrystallization of the BCC and FCC solid solutions take place at temperatures ranging from 120 to 550°C, and precipitation of second FCC1 phase and grain growth of equilibrium phases occur at higher temperatures. The BCC and FCC solid solution structure can be maintained even after the alloy was annealed at 1000°C. The alloy powder was successfully consolidated by pressure sintering at 800 °C with 5 GPa for 30 min. The sintered samples exhibit 9.5±0.2 GPa in Vickers hardness.

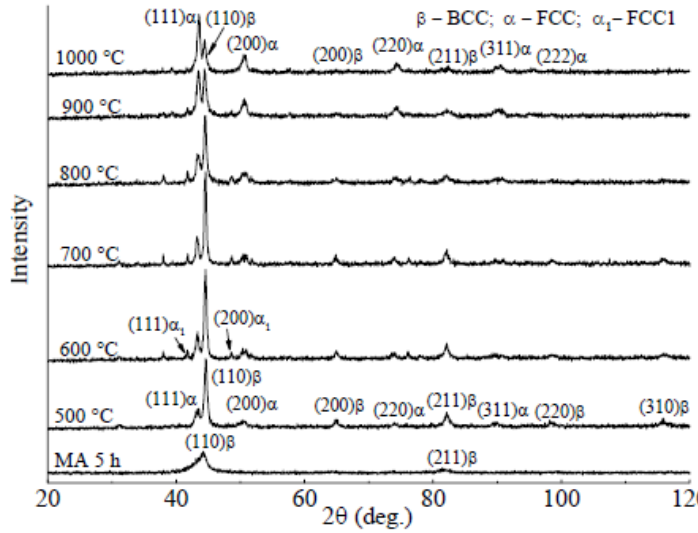

Fig. 3. XRD patterns of MA AlCuNiFeCr HEA powders after thermal annealing at different temperatures

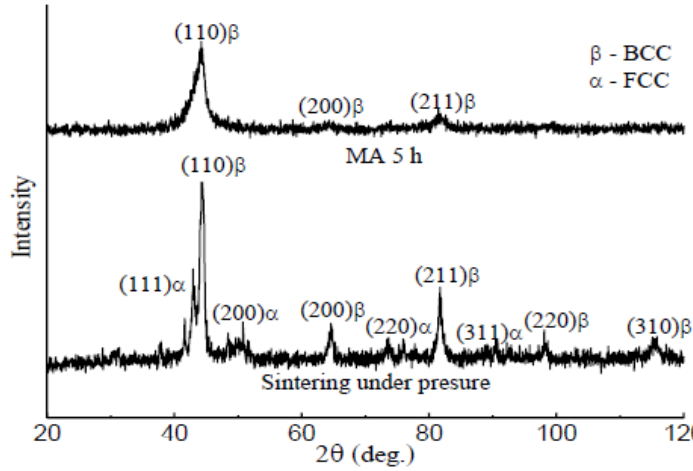

Fig. 4. XRD patterns of equiatomic AlCuNiFeCr HEA after MA and sintering at 800 °C with 5 GPa pressure for 0.5 h

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